MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE
NATIONAL TECHNICAL UNIVERSITY OF UKRAINE
"KYIV POLYTECHNIC INSTITUTE"

CHEMISTRY

Laboratory manual
for international students of the Faculty of Aerospace Systems
(specialities 134 - "Aviation and rocket and space machinery", 173 - "Avionics")

Approved by the Scientific Council of the ChTF NTUU "KPI"

Kyiv KPI 2016

Chemistry. Laboratory manual for international students of the Faculty of Aerospace Systems (specialities 134 - "Aviation and rocket and space machinery", 173 - "Avionics") / Comp.: O.O. Vasiliev. – K.: 2016. – 44 p.

Classified by the Scientific Council
of the Faculty of Chemical Technology NTUU "KPI"
(Minutes No. 11 *from* 26.12.*2016)*

Educational publication

CHEMISTRY

Laboratory manual
for international students of the Faculty of Aerospace Systems
(specialities 134 - "Aviation and rocket and space machinery", 173 - "Avionics")

Compiled by *Oleksandr Vasiliev*, candidate of chemical sciences, assistant professor

Managing Editor: *Oleksandr Andriiko*, doctor of chemical sciences, professor

Reviewer: *Grygorii Vasyliev*, candidate of technical sciences

Edited by compiler

Chemistry
Laboratory Manual
for International Students
of the Faculty of Aerospace Systems

Compiled by O.O. Vasiliev

Introduction

Laboratory experimnents are an inevitable part of Chemistry course that are used to fix and strengthen course theory and acquire practical chemical laboratory skills. This manual is intended as a guide on how to do the laboratory eperiments, perform nesessary calculations, and drew conclusions with an implication that certain amount of preparatory work must be done by the student prior to doing an experiment.

Typically, preparation for the laboratory experiment includes:

- understanding of theoretical material (absolute minimum is given in the Background sections of the experiments);
- familiarity with the protocol of experiment (according to the steps described in this manual);
- readiness to numerical calcualtions and results processing (done excersises and solved problems).

Basic requirements for the work

1. Students are permitted to do an experiment if they demonstrate a temlate of the Report for the experiment, which includes a protocol of experiment and formulas for processing its results.
2. Results of an experiment should be checked with an instructor before processing.
3. Completed report has to include:
    - title and objectives of the work;
    - protocol of the experiment;
    - results and observations;
    - detailed calcualtions and graphs (if required);
    - conclusions*.
4. Before starting the series of experiments students have to be instructed on the safety measures and sign the safety form.

*Conclusions should include a short summary of what was done in the experiment, what results were obtained and what patterns or laws they support.

Safety measures

1. It is strictly forbidden to perform any experiment that is not planed for the specific session or work in a laboratory alone.
2. Do not taste chemical reagents.
3. All experiments with concentrated alkali and acids, toxic and volatile substances must be carried out under the fume cupboard.
4. If concentrated acid or alkali got on the skin, immediately wash with large amount of running water and report to laboratory staff.
5. If any reagents got into the eyes, immediately rinse it with running water and report to laboratory staff.
6. Long hair and loose clothing must be confined while in a laboratory.
7. Appropriate clothing must be worn at all times while in the laboratory. Your legs must be completely covered below the knee by your choice of clothing. Only closed shoes with socks must be worn in the laboratory.
8. Before obtaining any chemicals carefully read the label on the reagent bottles.
9. Eating, smoking, and drinking are not allowed in a chemistry laboratory.
10. Thoroughly wash your hands after leaving the laboratory.
11. Never direct the open end of test tube toward yourself or anyone else.
12. Never pour water into concentrated acid.
13. Learn the proper procedure for igniting and operating a laboratory burner. Always extinguish the flame when the burner is not being used. Make sure that all flammable reagents are well removed before lighting the burner.
14. Use appropriate waste containers to dispose wastes after experiment is completed.
15. Never return unused chemicals to their original container (unless directed to do so by the instructor).
16. Securely replace lids, caps, and stoppers after removing reagents from containers.
17. Always wipe spatulas clean before and after inserting into reagent bottles.
18. Report any accident and/or injury, however minor, to your instructor immediately.
19. Never place anything that is not directly required for the experiment on laboratory desks; other items may interfere with the experiment.
20. Clean up any spill immediately.
21. Before leaving the laboratory, make sure your work area is cl ean and dry. Ensure that all gas, water, vacuum, and air valves are completely turned off.
22. Your instructor is available for any assistance you may need. Never hesitate to ask questions especially if there is any question concerning proper operating procedure. Be sure that you understand every instruction before proceeding.

Experiment # 1

Determining the amount of alkali in solution

Objectives: determine molar quantity of NaOH in aqueous solution using volumetric titration; verify the validity of the Law of Conservation of Matter.

Background

One of the most convenient ways to determine an amount of NaOH in aqueous solution is to use the reaction of its neutralization:

$$2\,\mathrm{NaOH} + \mathrm{H_2SO_4} \longrightarrow \mathrm{Na_2SO_4} + 2\,\mathrm{H_2O} \tag{1.1}$$

According to the eq. 1.1, when 2 mol of NaOH react with 1 mol H_2SO_4, 1 mol of sodium sulphate and 2 mol of water are formed.

***Mole*, [mol]** An amount of substance that contains as many elementary entities (e.g., atoms, molecules, ions, electrons) as there are atoms in 12 grams of pure carbon-12 (*Avogadro's number* $N_A = 6.02 \cdot 10^{23}\ \mathrm{mol}^{-1}$) .

***Molar Mass M*, [g/mol]** Mass of 1 mol of a substance:

$$M(X) = \frac{m(X)}{n(X)} \tag{1.2}$$

***Relative Molecular Mass (Molecular mass) M_r*, [u] or [D]** A sum of relative atomic masses (A_r) of atoms that constitute a molecule. For example, molecular mass of sulphuric acid

$$M_r(\mathrm{H_2SO_4}) = 2A_r(\mathrm{H}) + A_r(\mathrm{S}) + 4A_r(\mathrm{O}) = 2 + 32 + 4 \cdot 16 = 98\ \mathrm{D}.$$

Molecular Mass and Molar Mass (in g/mol) of a substance have different units, but same values. Thus,

$$M(H_2SO_4)[\text{g/mol}] = M_r(H_2SO_4)[\text{D}] = 98 \text{ g/mol}.$$

***Molar Concentration c(X),* [mol/l]** A ratio between amount of solute (dissolved substance) and volume of a solution:

$$c(X) = \frac{n(X)}{V(Solution)}.$$

Law of Conservation of Mass Whenever matter undergoes a change, the total mass of products of the change is the same as the total mass of reactants (within measurable limits):

$$\sum_i m(R_i) = \sum_i m(P_i) \tag{1.3}$$

where R_i – i-th reagent, P_i – i-th product.

Titration—an operation of gradual addition of a solution with known concentration to a solution with unknown concentration—is used to determine an amount of alkali in solution. It finishes in *equivalence point*, where all the alkali has reacted with the acid. Equivalence point is registered using *indicator* - a substance that has different colors depending on chemical surroundings (phenolphthalein in the titration of a base with an acid).

Procedure

Materials and Equipment

Equipment: standing support with a clamp, buret (V = 25 ml), funnel, two conical flasks (V=100 ml).

Chemicals: H_2SO_4 aqueous solution ($c(H_2SO_4)$= 0,05 mol/l), aqueous solution of NaOH, phenolphthalein.

Experimental

1. Obtain two flasks with an aqueous solution of NaOH from lab personnel

   NOTE

   Flasks are marked with numbers that correspond to your assignment. Write them down into the lab notebook.

2. Study the buret construction, paying special attention to its scale graduation values and the position of a glass bead inside a rubber tube.

3. Fill the buret with H_2SO_4 solution up to approx. 1/3 of its volume and learn how to release a liquid by pulling the wall of the rubber tube from the glass bead.

IMPORTANT

- use funnel to fill the buret with solution to avoid spilling;
- use acid solution with the same marking on the flask as is on the buret tag ($c(H_2SO_4)$= 0,05 mol/l)

4. Remove air bulbs from the glass buret ending by bending it upwards and releasing some amount of solution.

5. Fill the burett with the acid solution such that its level exceeds 0-th mark and release the excess until lower edge of liquid's meniscus is on the 0-th mark.

6. Begin the titration by slowly releasing H_2SO_4 solution from the buret to the NaOH solution in one of the conical flasks. Swirl the flask as you add the acid in order to efficiently mix the chemicals.

7. As equivalence point is approached, pink color will become less intensive; slow down and start adding H_2SO_4 solution **drop by drop**. Eventually the addition of just one drop of the acid will result in colorless solution in the conical flask. *Immediately stop adding the H_2SO_4 solution to the flask* as decoloration indicates that the equivalence point has been reached. Record the readings on the buret scale as

$V_1(H_2SO_4)$: _____ ml.

IMPORTANT

Remember to take buret readings on the lower edge of meniscus formed by H_2SO_4 solution.

8. Refill the buret with H_2SO_4 solution so that initial reading is zero, and then repeat the titration for the second sample of alkali solution. Record the readings as

$V_2(H_2SO_4)$: _____ ml.

TIP

you can pour the solution into the second (and, possibly, third) sample with steady flow up to a volume that is approximately one ml less than $V_1(H_2SO_4)$, and after that proceed accurately with *drop by drop* addition.

Proceed to (9), if the results satisfy *successful titration condition*:

$$|V_2(\mathrm{H_2SO_4}) - V_1(\mathrm{H_2SO_4})| < 0.2 \text{ ml} \tag{1.4}$$

Otherwise the titration must be performed on a third sample of NaOH solution. Clean one of the conical flasks, rinse it with water, and use it to obtain the sample that corresponds to your assignment number from lab personnel. Refill the buret again and repeat the titration.

9. When the Successful titration condition (eq. 1.4) is satisfied between any pair of the titration results, experiment is finished. Dispose the products of the titration from conical flasks and rinse them with running water.

Results processing

Calculations

1. Calculate average volume of the acid spent on NaOH neutralization and convert it to liters:

$$\bar{V}_{\mathrm{H_2SO_4}} = \frac{V_1 + V_2}{2} \cdot 10^{-3}.$$

2. Calculate the amount of $\mathrm{H_2SO_4}$ in the average volume, taking into account that $c(\mathrm{H_2SO_4})$= 0,05 mol/l:

$$n(\mathrm{H_2SO_4}) = c(\mathrm{H_2SO_4}) \cdot \bar{V}(\mathrm{H_2SO_4})$$

3. Using chemical equation of neutralization (eq. 1.1), calculate the amount of NaOH in solution and the amount of every product of the reaction:

$$n(NaOH) = 2n(\mathrm{H_2SO_4})$$

$$n(\mathrm{Na_2SO_4}) = n(\mathrm{H_2SO_4})$$

$$n(\mathrm{H_2O}) = n(NaOH) = 2n(\mathrm{H_2SO_4})$$

4. Calculate the mass of every substance taking part in the reaction using eq. 1.2 and show, that relation eq. 1.3 holds.

Conclusions

TIP

Try to answer these questions in your conclusion:

- How can we chemically determine an amount of a substance in solution?
- How can we establish the moment, when all the alkali has reacted?
- How does total mass of substances change during a chemical reaction?

Experiment # 2

Classes of inorganic compounds

Objectives: getting familiar with methods of formation of insoluble hydroxides, neutral, acid and base salts and their basic chemical properties.

Procedure

Materials and Equipment

Equipment: rack with test tubes, Kipp's apparatus loaded with HCl and $CaCO_3$.

Chemicals: salt *A* and *B* solutions (from tbl. 2.1 according to assignment), NaOH aqueous solution; aqueous solutions of $CdSO_4$, $BaCl_2$, $Pb(NO_3)_2$, Na_2S, Na_2SO_4, KI, Na_2CO_3, Na_3PO_4, $CoCl_2$ (or $Co(NO_3)_2$); CuO and P_2O_5 powders, aqueous solutions of HCl and $Ca(OH)_2$.

Table 2.1: Experiment assignments

Assignment	Salt A	Salt B
1	$Cd(NO_3)_2$	$Pb(NO_3)_2$
2	$MgSO_4$	$Cr_2(SO_4)_3$
3	$NiSO_4$	$Al_2(SO_4)_3$
4	$CuSO_4$	$ZnSO_4$
5	$MnSO_4$	$SnSO_4$
6	$FeCl_3$	$Al(NO_3)_3$

Experimental

1. Insoluble Hydroxides

a) Put 1-2 ml of salt *A* solution into a test tube and add several droplets of NaOH avoiding excess until insoluble hydroxide is formed; mark the color of the precipitate.

b) Stir the test tube content (the precipitate has to stay insoluble) and divide it into two parts. Add nitric acid solution (HNO_3) into one part and sodium hydroxide solution into the second part.

c) write down the equations of chemical reactions, observations and conclusions about chemical nature of the hydroxide (base or amfoteric) into your report.

d) Repeat steps 1 through 3 with the solution of salt *B*.

2. Neutral Salts

Reaction of salts between each other

a) Put 1-2 ml of $CdSO_4$ solution into a test tube and add about 1 ml of Na_2S; write the equation of chemical reaction and mark the color of the precipitate, that has been formed.

b) Repeat step 1 for $BaCl_2$-Na_2SO_4 and $PbNO_3$-KI pairs of solutions.

Reaction between salt and acid

Mix 1-2 ml of $PbNO_3$ solution with 1 ml of {sulf} in a test tube; write the equation of chemical reaction (mark which compond forms precipitate) and observations.

Reaction between salt and alkali

Add 1-2 ml of $Ca(OH)_2$ and 1-2 ml of Na_2CO_3 into a test tube; write the equation of chemical reaction (mark which compond forms precipitate) and observations.

Reactions of salt formation with oxides

a) Put small amount of copper (II) oxide (CuO) into a test tube, add 1-2 ml of hydrochloric acid (HCl); write the equation of chemical reaction and observations.

b) Pour 1-2 ml of calcium hydroxide ($Ca(OH)_2$) solution into a test tube and put small amount of P_2O_5, using a dry glass stick; write the equation of chemical reaction and observations.

3. Acid and Base Salts

Acid salt preparation

Pass CO_2 gas fromm Kipp's apparatus through 2-3 ml of lime water ($Ca(OH)_2$ aqueous solution). Observe $CaCO_3$ precipitate formation with its subsequent dissolution in abundance of carbonic acid (H_2CO_3) with calcium bicarbonate ($Ca(HCO_3)_2$) formation; write the equation of chemical reaction and observations.

IMPORTANT

Save the solution for further use.

Chemical properties of acid salts

Split calcium bicarbonate solution from previous experiment (Acid salt preparation) into 4 parts in separate test tubes, and proceed as follows:

- First tube: heat until its content boils;
- Second tube: add $Ca(OH)_2$ solution;
- Third tube: add Na_2CO_3 solution;
- Fourth tube: add Na_3PO_4 solution;

Write down the equation of every reaction and corresponding observations.

Base salt preparation

Pour into a test tube 2-3 ml of $Co(NO_3)_2$ and add by droplets and with continuous stirring diluted solution of NaOH; write the equation of chemical reaction and observations.

IMPORTANT

Save the product for further use.

Chemical properties of base salts

Split $[Co(OH)]NO_3$ (violet-blue precipitate) from previous experiment (Base salt preparation) into two parts in separate test tubes, and proceed as follows:

- First tube: add 1 ml of nitric acid (HNO_3);
- Second tube: add an excess of NaOH solution;

Write down the equation of every reaction and corresponding observations.

Conclusions

TIP

Try to answer these questions for every class of compounds (insoluble hydroxides, neutral salts, acid salts, base salts):

- What reactions can be used to obtain the compounds?
- What chemical properties do compounds of the class posses (use substances from your experiment as examples) and what are the reasons to think so?

Experiment # 3

The heat of neutralizations

Objectives: Determine in experiment the heat of neutralization of strong acid with strong base

Background

***Heat of reaction*, [kJ]** Sum of all types of energy, that is absorbed or produced during chemical reaction.

The heat of reaction under constant temperature and pressure is the change of enthalpy of the reaction ΔH. If energy is absorbed ($\Delta H > 0$); drop of temperature in surroundings) the reaction is called *endothermic*. If energy is produced ($\Delta H < 0$); rise of temperature in surroundings) the reaction is called *exothermic*.

Thermochemical equation Chemical equation, which includes the state of matter of reactants and the heat of reaction for the amounts of reactants, given by stoichiometric quotients.

NOTE

State of matter notations:

- X(g) - gaseous;
- X(l) - liquid;
- X(s) - solid;
- X(aq) - aqueous solution,
  where X is a chemical formula of a substance.

Standard heat of neutralization is the heat of reaction between one mole of hydrogen ions and one mole of hydroxide ions with formation of one mole of water molecules:

$$H^+ + OH^- \longrightarrow H_2O, \quad \Delta_n H^0 = -57.3 \text{ kJ}.$$

$\Delta_n H^0 = -57.3$ kJ is the heat of neutralization under standard conditions (T =298.15 K, P = 101.3 kPa).

Procedure

Materials and equipment

Equipment: standing support with a clamp, burette, calorimeter, graduated cylinder (V = 50 ml), thermometer.

Chemicals: sulfuric acid solutions ($c(H_2SO_4)$ = 0.5 mol/l and $c(H_2SO_4)$ = 1 mol/l), NaOH solution with c(NaOH) = 1 mol/l.

Experimental

1. Get molar concentration and volume of acid solution to use in the experiment from the instructor.

Table 3.1: Initial data

Acid			Base		
V_a, l	c_a, mol/l	ρ_a, g/l	V_b, l	c_b, mol/l	ρ_b, g/l

2. Calculate the amount of the acid in the volume of solution:

$$n_a = c_a \times V_{\text{solution}} \tag{3.1}$$

3. Write the equation of reaction between acid and alkali.
4. Using the equation of reaction, calculate the amount of NaOH to completely neutralize the acid and volume of its solution to use (see eq. 3.1).
5. Fill the burette with acid solution and measure the assigned volume (see step 1) into inner beaker of the calorimeter. Measure temperature of the solution with thermometer and write it down into report as t_1.
6. Using a graded cylinder, measure previously calculated volume of NaOH solution and add it to acid solution in the inner beaker. Continuously mixing the solution

(use termometer), observe temperature change on the termometer. Write down into the report maximum temperature it shows as t_2.

Calculations

1. Determine the temperature difference during the neutraliztion:

$$\Delta t = t_2 - t_1.$$

2. Calculate the sum of masses of two solutions, using densities of solutions (get density values from the instructor):

$$m_{\text{solution}} = m_{\text{a}} + m_{\text{b}} = V_{\text{a}} \cdot \rho_{\text{a}} + V_{\text{b}} \cdot \rho_{\text{b}}$$

3. Calculate the heat of specific neutralization process (assume the heat capacity of the solution is the same as that of water $C(\text{H}_2\text{O}) = 4.18$ J/g $\cdot$ K:

$$\Delta H_r = m_{sol} \cdot \Delta T \cdot 4.18 \cdot 10^{-3} \qquad \text{kJ/g} \cdot \text{K}.$$

4. Taking into account that the amount of water is equal to the amount of alkali (from the equation of reaction), find experimental standard heat of neutralization:

$$\Delta_n H^\circ_{exp} = \frac{\Delta H_r}{n(NaOH)} \qquad \text{kJ/mol}.$$

5. Calculate an absolute and relative errors of experiment and write them into report:

$$\Delta = |\Delta_n H^\circ_{theor} - \Delta_n H^\circ_{exp}|;$$

$$\delta = \frac{\Delta}{|\Delta_n H^\circ_{theor}|} \cdot 100\%.$$

Table 3.2: Report

t_1, °C	t_2, °C	Δt	m, g	$\Delta_n H^\circ_{exp}$, kJ/mol	Δ, kJ/mol	δ, %

Conclusions

TIP

Try to answer this questions in your conclusion:

- What is common and central for all neutralization reactions?
- How is the heat of reaction measured?
- Does the heat of neutralization depend on what substances react?
- Explain main reasons for the errors in your experiment.

Experiment # 4

Dependance of the rate of chemical reaction on concentration of reactants and temperature

Objectives: Determine the dependence of the rate of reaction

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + S + SO_2 + H_2O$$

on concentration of sodium thiosulphate ($Na_2S_2O_3$) and the temperature.

Background

Chemical reactions can occur in heterogeneous and homogeneous systems.

Homogeneous system A system consisting of only one phase, a reaction takes place in the entire volume of reacting mixture.

All reactions between gases or in solutions are homogeneous.

Heterogeneous system A system, that consists of several distinct phases. Chemical reactions in such systems take place on the interface between two phases.

An example of the heterogeneous process is rusting of steel or any other corrosion processes.

Rate of chemical reaction The number of basic interactions between reactants, which result in product formation in a unit of volume (homogeneous r.) or surface (heterogeneous r.) per unit of time.

The *rate of chemical reaction* is most often defined as change in concentration of reaction participant X with time τ:

$$v = \pm\frac{\mathrm{d}c(\mathrm{X})}{\mathrm{d}\tau} \qquad mol/(l \cdot s),$$

where "–" signifies, that X is a reactant and "+", that it is a product.

According to *the Law of acting masses*,

> the reaction rate is proportional to the product of reactants *concentrations* raised to the powers of their stoichiometric coefficients.

Thus, for the model reaction

$$\mathrm{a\,A} + \mathrm{b\,B} \longrightarrow \mathrm{c\,C} + \mathrm{d\,D},$$

this proportionality, which is called *kinetic equation of the reaction* has the form:

$$v = k \cdot c_{\mathrm{A}}^{\mathrm{a}} \cdot c_{\mathrm{B}}^{\mathrm{b}}.$$

For the reaction in study:

$$v = k \cdot c(\mathrm{Na_2S_2O_3}) \cdot c(\mathrm{H_2SO_4}).$$

> NOTE
>
> Original formulation of *the Law of acting masses*:
>
> *the rate of any chemical reaction is proportional to the product of the masses of the reacting substances, with each mass raised to a power equal to the coefficient that occurs in the chemical equation.*
>
> Thus, it is the Law of acting *masses*, not *concentrations*.

The proportionality quotient k in a kinetic equation is called *reaction rate constant*. It is the rate of reaction when reactant concentrations are 1 mol/l. The constant depends on reactant's nature, temperature and catalyst but, unlike the rate of reaction, it doesn't depend on the concentration of the reactants.

The rate of reaction and rate constant rise with temperature in accordance with empirical *Van't Hoff's rule*.

Van't Hoff's Rule The rate of chemical reaction increases two- to fourfold for each rise of 10 °C in temperature:

$$\frac{v_2}{v_1} = \gamma^{\Delta T/10} \quad \text{or} \quad \frac{k_2}{k_1} = \gamma^{\Delta T/10},$$

$v_1(k_1)$, $v_2(k_2)$ – rates (rate constants) at temperatures T_1 and T_2, respectively;
ΔT – change in temperature;
γ – temperature coefficient of reaction – *the value, which shows in how many times the rate of a particular reaction changes every 10 °C.*

The dependence of the rate of reaction on temperature is given more rigorously by *the Arrhenius equation* through the rate constant.

The Arrhenius Equation

$$k = A \cdot e^{-E_A/(RT)},$$

where $A = pz_0$ – *pre-exponential factor (prefactor)*, it doesn't depend on temperature;
z_0 – frequency of collisions of molecules;
p – steric factor, which determines proper orientation of molecules during the collision;
$R = 8.31 \cdot 10^{-3}$ kJ/(mol · K) – universal gas constant;
T – absolute temperature;
E_A – activation energy, kJ/mol.

Activation Energy E_A, [kJ/mol] A minimal excessive energy relative to mean energy of molecules at given temperature, that is needed for the chemical interaction between the molecules to occur.

The *activation energy* is spent on mitigation or breaking of the chemical bonding between atoms and on transition of the molecules into activated state. The bigger the activation energy, the smaller is the rate of reaction and the rate constant.

The Arrhenius equation in logarithm form:

$$\ln k = \ln A - E_A/(RT),$$

and the dependence of $\ln k$ from *1/T* is linear. Thus, *activation energy* can be calculated from such dependence as tangent of its slope (α) to *1/T*:

$$E_A/(RT) = \mathrm{tg}\alpha = \Delta \ln k/\Delta(1/T).$$

As $\Delta \ln k = \ln k_2 - \ln k_1 = \ln \frac{k_2}{k_1}$, from Van't Hoff's rule:

$$\Delta \ln k = \ln \frac{k_2}{k_1} = \ln \gamma^{\Delta T/10}.$$

Taking into account two previous equations:

$$E_A = \frac{RT_1T_2}{T_2 - T_1} \ln \gamma^{\Delta T/10}.$$

Procedure

Materials and equipment

Equipment: buret with sodium thiosulfate ($c(Na_2S_2O_3) = 0.1$ mol/l), buret with distilled water H_2O, thermostats (40 and 60 °C), graduated cylinder, numbered beakers, test tubes, stopwatch.

Chemicals: sodium thiosulfate solution with $c(Na_2S_2O_3) = 0.1$ mol/l), distilled water H_2O, sulphuric acid H_2SO_4 ($c(H_2SO_4) = 1$ mol/l).

Experimental

Rate dependence on the reactants concentration

1. Pour assigned volumes of solution (see tbl. 4.1) from buret with $Na_2S_2O_3$ into three numbered beakers. From the buret with H_2O add assigned volumes of water.
2. Measure with graduated cylinder three portions of H_2SO_4 into three clean test tubes.

Table 4.1: Assignments

Assignment	$V(Na_2S_2O_3)$, ml (a)	$V(H_2O)$, ml (b)	$V(H_2SO_4)$, ml (c)
1	5	10	10
	10	5	10
	15	0	10
2	10	20	10
	20	10	10
	30	0	10
3	5	15	10
	10	10	10
	20	0	10
4	5	20	10
	10	15	10
	25	0	10
5	5	20	15
	10	10	15
	20	5	15

Assignment	$V(Na_2S_2O_3)$, ml (a)	$V(H_2O)$, ml (b)	$V(H_2SO_4)$, ml (c)
6	4	16	15
	12	8	15
	20	0	15
7	8	12	10
	12	8	10
	20	0	10

3. Simultaneously pour sulphuric acid solutions from test tubes into beakers with thiosulfate solution and start the stopwatch; mark the times, when opalescence start to appear in every beaker in the report.

Rate dependence on temperature

1) Pour 5 ml of $Na_2S_2O_3$ solution into a test tube and 5 ml of H_2SO_4 into the other test tube. Mix sulfuric acid solution with sodium thiosulphate under room temperature and turn on the stopwatch. Fix the time, when opalescence starts to occur and write it into the report together with current room temperature.
2) Use 40 °C thermostat to heat up test tubes, prepared as in step 1, by keeping them in hot water for 5 min. Mix sulfuric acid solution with sodium thiosulphate without taking the tube with $Na_2S_2O_3$ from water (elevate it a little, so the opalescence can be observed without obstacles) and measure the time of reaction. Write the time into the report, together with thermostat's thermometer readings (they may deviate from 40 °C).
3) Repeate step 2 with 60 °C thermostat.

Calculations

Rate dependence on the reactants concentration

1) Calculate the concentration of sodium thiosulfate in every beaker:

$$c(Na_2S_2O_3) = \frac{0.1a}{a+b+c},\ \text{mol/l}.$$

2) Calculate the concentration of sulfuric acid in the volume of reacting mixture:

$$c(H_2SO_4) = \frac{0.1a}{a+b+c},\ \text{mol/l}.$$

3) Calculate relative rates of reaction in every beaker:

$$v = \frac{100}{\tau},\ \mathrm{s}^{-1}$$

4) Calculate simulated reaction rate constant for every $Na_2S_2O_3$ concentration and its mean value:

$$k = \frac{v}{c(Na_2S_2O_3) \cdot c(H_2SO_4)};$$
$$\bar{k} = \frac{k_1 + k_2 + k_3}{3}.$$

5) Draw the diagram "Rate of reaction vs Concentration"

TIP
To check if you have drawn the diagram correctly, consider the following:

$$v = kc(Na_2S_2O_3)c(H_2SO_4).$$

If we are keeping $c(H_2SO_4)$ constant, than the kinetic equation in algebraic form (y is a rate and x is a concentration of $Na_2S_2O_3$) is

$$y = kx,$$

which is an equation of a straight line going through zero.

Table 4.2: Report

Beaker	$c(Na_2S_2O_3)$, mol/l	τ, s	$\frac{100}{\tau}$, s^{-1}	k
1				
2				
3				

Rate dependence on temperature

1) Calculate relative rates (rates proportional to real) under every studied temperature:

$$v_t = \frac{100}{\tau_t},\ s^{-1}.$$

2) Draw the diagram "Rate of reaction vs Temperature"
3) Calculate temperature coefficient of reaction rate for every temperature range and its mean value:

$$\gamma_1 = \sqrt[\frac{\Delta T}{10}]{\frac{v_2}{v_1}}, \qquad \Delta T = T_2 - T_1;$$

$$\gamma_2 = \sqrt[\frac{\Delta T}{10}]{\frac{v_3}{v_2}}, \qquad \Delta T = T_3 - T_2;$$

$$\gamma_3 = \sqrt[\frac{\Delta T}{10}]{\frac{v_3}{v_1}}, \qquad \Delta T = T_3 - T_1;$$

$$\bar{\gamma} = \frac{\gamma_1 + \gamma_2 + \gamma_3}{3}.$$

4) From the Arrhenius equation calculate activation energy of the reaction:

$$E_A = \frac{T_x T_1}{T_x - T_1} R \ln \bar{\gamma}^{\Delta T/10}.$$

5) Fill in the Report table (tbl. 4.3).

Table 4.3: Report

t, °C	T, K	τ, s	v_i, s^{-1}	γ	E_A, kJ/mol
(~20) ____					
(~40) ____					
(~60) ____					

Conclusions

TIP
Try to answer this questions in your conclusion:

- What is the character of the reaction rate dependence from concentration?
- What physical meaning does constant of reaction have?
- How does rate of reaction depend on temperature?
- What can be the explanation for greater reaction rates at higher temperatures?

Experiment # 5

The heat of dissolution

Objectives: study the heat of a process, using the solution as an example.

Background

When a process takes place at constant temperature and pressure, its heat is measured as the change of thermodynamic function *enthalpy* of the system, ΔH.

The heat of a process The quantity of energy, which is produced or absorbed during the process as heat.

Standard Enthalpy of formation $\Delta_f H^0$**,** **[kJ/mol]** The heat of formation of 1 mole of a compound from its constituent elements, with all substances in their standard states at pressure of 1 atmosphere (1 atm or 101.3 kPa).

Standard enthalpy of dissolution $\Delta_s H^0$**,** **[kJ/mol]** The enthalpy change associated with the dissolution of 1 mole of a substance in a solvent at 1 atmosphere (1 atm or 101.3 kPa).

The dissolution process consists of several physical and chemical phenomena:

1) breaking of intermolecular and chemical bonds in the solute, which demands energy ($\Delta H_1 > 0$);
2) chemical interaction between the particles of the solute and the solvent, where energy is released as a result of new bonds being formed ($\Delta H_2 < 0$).

Depending on the magnitude of effects on stages 1 and 2 dissolution can be exothermic or endothermic. When $|\Delta H_1| < |\Delta H_2|$, there is an excess of energy, which is released into surroundings as heat, producing temperature rise. Otherwise, when $|\Delta H_1| < |\Delta H_2|$, the $\Delta_s H > 0$ and the temperature of surroundings falls. For most solids the latter is true.

Procedure

Materials and equipment

Equipment: thermometer, simplified calorimeter, graded cylinder (50-100 ml).

Chemicals: distilled water, crystalline $H_2C_2O_4$, $K_2Cr_2O_7$, Na_2CO_3, $Na_3PO_4 \cdot 12\,H_2O$, $Na_2B_4O_7 \cdot 10\,H_2O$, NaOH, NH_4Cl, KOH.

Experimental

1. Obtain a number of an assignment from the instructor:

Table 5.1: Assignments

No.	Formula	$V(H_2O)$, ml	$\Delta_s H^0$, kJ/mol
1	$H_2C_2O_4$	50	36
2	$K_2Cr_2O_7$	50	70
3	Na_2CO_3	50	-24
4	$Na_3PO_4 \cdot 12\,H_2O$	25	60
5	$Na_2B_4O_7 \cdot 10\,H_2O$	25	108
6	NaOH	50	-42
7	NH_4Cl	25	15
8	KOH	25	-54

2. Pour the water (assigned volume) into the internal beaker of the simplified calorimeter and measure the temperature t_1 °C; write it into the report.
3. Put the crystals of the substance into the water. Carefully mix the system with the thermometer until the substance is fully dissolved and mark the temperature maximum or minimum t_2 °C; write it into the report.

CAUTION
Simplified calorimeter is only a crude approximation of an isolated system in which a heat of a process should be measured. Actually, it is an open system, and both transfer of matter and transfer of energy are possible. The less time is spent during the measurement the less interaction system has with the surroundings and the results are more correct. Hence, try to be as fast as possible (while keeping all the precautions required) with dissolution process.

Calculations

1. Calculate the amount of heat transfered during dissolution:

$$q = 4.18 \cdot 10^{-3} \cdot \Delta t \cdot m_{solution}.$$

NOTE
Several approximate assumptions are made in the equation above:

- $m_{solution} = m(\mathrm{H_2O}) = V(\mathrm{H_2O})$ as $\rho(\mathrm{H_2O}) = 1$ g/ml;
- The heat capacity of the solution is equal to that of water $C_{sol} = 4.18 \cdot 10^{-3}$ J/(g $\cdot$ K).

2. Calculate the mass of the solute, using standard enthalpy of solution for the solute from the tbl. 5.1 and its molar mass:

$$m(X) = \frac{-q}{M(X) \cdot \Delta_s H^0(X)}.$$

3. Write down all the results into the report.

Table 5.2: Report

Formula	t_1, °C	t_2, °C	Δt, °C	q, kJ	M(X), g/mol	m, g

Conclusions

TIP
Try to answer these questions in your conclusion:

- What factors influence the sign of the heat of solution and which one was more significant in your case?
- Why can't the mass of solute, determined as a result of the experiment be precisely equal to the mass of the specimen you received for the study?

Experiment # 6

Reactions in solutions

Objectives: study main reasons for the ion exchange reactions in electrolytesolutions to occur.

Background

On mixing of solutions of different electrolytes an association of ions of opposite charge becomes possible and may lead to the formation of

- poorly soluble electrolyte (salt, hydroxide);
- soluble weak electrolyte (weak acid, NH_4OH etc.) or water;
- gaseous non-electrolyte (CO_2, SO_2 etc.).

Ion exchange reactions Chemical reactions in which ions from one electrolyte are transfered to another electrolyte.

Ion exchange reactions are very fast, as ions in solutions are already activated by solvent molecules, which behave as homogeneous catalyst.

Ion exchange reactions are typically represented by molecular, complete ionic and net ionic equations.

Molecular equation Shows the full formula for each substance involved (or the full name of each substance), without reference to a substance being ionic or molecular. Information on electrolyte strength may be shown underneath the formula and state of matter of gaseous and poorly soluble substances wtih $\uparrow$ and $\downarrow$:

$$\underset{\text{Strong}}{2\,AgNO_3} + \underset{\text{Strong}}{CaCl_2} = \underset{\text{Weak}}{2\,AgCl\downarrow} + \underset{\text{Strong}}{Ca(NO_3)_2}.$$

Complete ionic equation Shows strong electrolytes in dissociated form (i.e. as ions) and weak electrolytes and non-electrolytes as molecules, including the state of matter of the latter:

$$2\,Ag^+ + 2\,NO_3{}^- + Ca^{2+} + 2\,Cl^- = 2\,AgCl\downarrow + Ca^{2+} + 2\,NO_3{}^-.$$

Net ionic equation Ions, which are present on both sides of the complete ionic equation ("spectator" ions) are excluded from it, leaving only the species interactiong during the reaction:

$$Ag^+ + Cl^- = AgCl\downarrow.$$

Procedure

Materials and equipment

Equipment: rack with test tubes, fume cupboard.

Chemicals: aqueous solutions of Na_2SO_4, Na_2SO_3, $BaCl_2$, HNO_3, $Pb(NO_3)_2$, NaCl, KI, Na_2S.

Experimental

Formation of poorly soluble electrolytes during ion-exchange reactions

Pour 0.5-1 ml of sodium sulfate Na_2SO_4 and sodium sulfite Na_2SO_3 solutions into separate test tubes. Add 2-3 drops of barium chloride $BaCl_2$ into both tubes.

CAUTION: Save the products of reactions for further use.

Write down the observations into the report and compose molecular, complete ionic and net ionic equations of the reactions.

Dissolution of poorly soluble electrolytes during chemical interaction

Add 3-5 drops of HNO_3 solution into the tubes with poorly soluble barium salts from previous step. Write down the observations into the report and compose molecular, complete ionic and net ionic equations of the reactions.

Equilibrium shift in reactions of electrolyte solutions

1) Pour 1 ml of lead nitrate $Pb(NO_3)_2$ solution into a test tube and add the same volume of sodium chloride NaCl solution. Write down the observations into the report and compose molecular, complete ionic and net ionic equations of the reactions.

> CAUTION
> Every subsequent step of this part of the experiment requires the products of previous step. Only the products of third step should be disposed as a waste.

2) Add several drops of potassium iodide KI solution to the products of the previous step. Write down the observations into the report and compose molecular, complete ionic and net ionic equations of the reactions.

3) Add Na_2S solution to the products of the previous step. Write down the observations into the report and compose molecular, complete ionic and net ionic equations of the reactions.

> CAUTION
> There is a high probability of formation of the toxic H_2S during this step, thus it should be done in a fume cupboard.

Conclusions

> TIP
> Try to answer these questions in your conclusion:

- What are the reasons for the reactions between sodium sulfate, sodium sulfite and barium chloride to occur?
- Why does one of the poorly soluble barium salts dissolves in HNO_3, while the other withstands the interaction?
- Why do new poorly soluble products keep forming on every subsequent step of the last part of the experiment?
- What is the direction of equilibrium shift in reactions of electrolyte solutions?

Experiment # 7

pH-metric determination of the dissociation degree and constant

Objectives: study the rates of dissociation of strong and weak acids and the constant of dissociation of weak acid, using precise measurements of the pH of acid solutions.

Background

Upon the solution of electrolytes in water occurs the phenomenon of their *electrolytic dissociation*.

Electrolytic dissociation Breaking of electrolytes' molecules into constituent ions (cation and anion) under the influence of polar molecules of solvent (most often water).

Strong electrolytes dissociate completely and irreversibly. Thus, there are no molecules in the solutions of strong electrolytes, there are only ions.

Weak electrolytes dissociate partially and reversibly.

Dissociation degree, α A number that shows how many of the initial molecules dissociated into ions:

$$\alpha = \frac{N_{dissociated}}{N_{initial}} = \frac{[dissociated]}{c_{initial}}.$$

(Equilibrium concentration is denoted as [ ].)

The larger is the α, the stronger is an electrolyte, and for strong electrolytes the dissociation degree is equal to one. Upon heating or dissolution the dissociation degree of a weak electrolyte increases (in accord with Le Chatelier principle).

The concentration of any ion, produced during the dissociation, is:

$$c_{ion} = \alpha \cdot n \cdot c_{initial},$$

where n is the quantity of ions of certain type.

As the dissociation of weak electrolytes is reversible, both molecules and ions are always present in equilibrium:

$\mathrm{HA} \rightleftarrows \mathrm{H^-} + \mathrm{A^-}$	weak monobasic acid,
$\mathrm{KatOH} \rightleftarrows \mathrm{Kat^+} + \mathrm{OH^-}$	weak monoacid base.

Dissociation Constant, K Equilibrium constant of the dissociation process.

For weak monobasic acid:

$$K = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}.$$

For weak monoacid base:

$$K = \frac{[\mathrm{Kat^+}][\mathrm{OH^-}]}{[\mathrm{KatOH}]}.$$

The dissociation constant depends on temperature and does not depend on concentration.

The dissociation degree and the constant of dissociation are related by *Ostwald dilution law.*

Ostwald dilution law

$$K = \frac{\alpha^2 \cdot c_0}{1 - \alpha},$$

or, for very weak electrolytes with $\alpha << 1$:

$$K = \alpha^2 \cdot c_0,$$

where c_0 is the initial concentration of an electrolyte.

Procedure

Materials and equipment

Equipment: pH-meter, 100 ml volumetric flask, filter paper, 50 ml beakers.

Chemicals:* HCl, CH_3COOH aqueous solutions (c=0.01 mol/l), distilled water.

Experimental

1. Study the pH-meter manual.
2. Using the pH-meter measure pH of HCl and CH_3COOH with $c = 0.01$ mol/l. To do this, pour the solution into a beaker, immerse electrodes and conduct measurements according to the device's manual. Write down the results into the report.
3. Pour the volume V_0 of acetic acid given by instructor into volumetric flask and fill it with distiled water up to the mark. Seal the flask and mix the solution by turning the flask upside down several times. Calculate the concentration of the new solution from the relation:
$$V_0 \cdot 0.01 = c_1 \cdot 100.$$
4. Measure the pH of the solution and write it into report (procedure is similar to that in step 2).

Calculations

1. Calculate the degree of dissociation of the hydrochloric and acetic acids' solutions with $c = 0.01$ mol/l and in the acetic acid solution with c_1:
$$\alpha = \frac{[H^+]}{c}.$$
2. Using the Ostwald dilution law, calculate dissociation constant for the CH_3COOH solutions with $c = 0.01$ mol/l and c_1:
$$K = \frac{\alpha^2 \cdot c}{1 - \alpha},$$
and take arithmetic mean of both values.
3. Write down the equations of dissociation of HCl and CH_3COOH and the expression for acetic acid dissociation constant.

Table 7.1: Report

Acid	c, mol/l	pH	pOH	$[H^+]$	$[OH^-]$	α	K
HCl	0.01						
CH_3COOH	0.01						
CH_3COOH							
$V_0 =$ ____							

Conclusions

TIP
Try to answer these questions in your conclusion:

- What is the difference between weak and strong electrolytes?
- How does the degree of dissociation depend on concentration?
- How does the constant of dissociation depend on concentration?

Experiment # 8

Electrochemical systems: Galvanic cell, electrolysis and electrochemical corrosion

Objectives: study the construction and principles of operation of a simple galvanic cell using Daniel's cell as working example, determine the electromotive force, voltage and polarization of the cell; study the process of electrolysis in aqueous solutions of salts; learn the conditions in which microscopic corrosive electrochemical cells appear and work and the influence of various factors on the rate of electrochemical corrosion.

Background

Galvanic (Voltaic) Cell

Galvanic cell* or *Voltaic cell An electrochemical cell in which the energy of spontaneous redox reaction is transformed into electrical energy. It consists of two electrodes (half-cells) connected by a wire with electrolytes being divided by ion-permeable membrane or ion-conducting salt bridge.

Anode Electrode with lower value of electrochemical potential where oxidation process takes place.

Cathode Electrode with higher value of electrochemical potential; reduction occurs on the cathode.

Anode and cathode immersed into electrolyte solutions and connected by a wire form *external half-circuit* of the galvanic cell. Electrons move from the anode to the cathode through the external half-circuit. Electrolyte solutions, divided by an electrolytic key to prevent mixing of solutions but keep ionic conductivity, together with the electrodes form

internal half-circuit of the galvanic cell. Ions move between the anode and the cathode through the internal half-circuit.

The Galvanic cell's construction is typically written down as simplified scheme:

$$(-) \quad \mathrm{S}_a \mid \mathrm{El}_a \parallel \mathrm{El}_c \mid \mathrm{S}_c \quad (+)$$

where $\mathrm{S_a}$, $\mathrm{S_c}$ – solid (or solid with absorbed gas) part of the anode (a) and cathode (c); $\mathrm{El_a}$, $\mathrm{El_c}$ – electrolytes of the anode and cathode respectively; $\mid$ – solid-liquid boundary; $\parallel$ – salt bridge or ion-permeable membrane.

For example, if both the anode and the cathode are metallic electrodes of the first type, the scheme is

$$(-) \quad {\mathrm{Me_a}}^0 \mid {\mathrm{Me_a}}^{n+} \parallel {\mathrm{Me_c}}^{m+} \mid {\mathrm{Me_c}}^0 \quad (+), \tag{8.1}$$

and the electrode processes (half-reactions) are

Anode:	${\mathrm{Me_a}}^0 \longrightarrow {\mathrm{Me_a}}^{n+} + \mathrm{ne}^-$	oxidation
Cathode:	${\mathrm{Me_c}}^{m+} + \mathrm{me}^- \longrightarrow {\mathrm{Me_c}}^0$	reduction.

The maximum useful work that can be done in the galvanic cell due to the redox reaction is given by the formula:

$$-\Delta G = nFE,$$

where F is the Faraday constant, $F = 96500$ C/mol; E is an electromotive force of the galvanic cell, V.

Electromotive force, E **[V]** The difference between the potentials of two electrodes, the cathode and the anode:

$$E = \varphi_{cathode} - \varphi_{anode}. \tag{8.2}$$

The experimental difference between the potentials of cathode and anode (or voltage U) is always smaller than the electromotive force due to polarization of the electrodes.

Electrochemical polarization , η A shift of electrode potentials due to the change in concentration of electrolytes near the electrodes.

$$\eta = E - U. \tag{8.3}$$

Electromotive force under standard conditions can be calculated using standard electrode potentials, which are most often tabulated at 25 °C.

Standard electrode potential The electromotive force of the galvanic cell, composed of given electrode in standard conditions (electrolyte concentration 1 mol/l; gas pressure 1 atm.) and the standard hydrogen electrode ($\varphi^0_{H^+ / H_2{}^0} = 0\ V$).

To calculate the potential of an electrode in *non-standard conditions Nernst equation* is used*:

$$\varphi = \varphi^0 + \frac{RT}{nF} \ln \frac{[\text{Oxidized form}]}{[\text{Reduced form}]}.$$

As most calculations are done under room temperature, transforming natural logarithm into common (to base 10) logarithm and aggregating constants gives:

$$\varphi = \varphi^0 + \frac{0.059}{n} \lg \frac{[\text{Oxidized form}]}{[\text{Reduced form}]}.$$

In the case of metal electrodes of the first type (metal plate put into the solution containing cations of this metal; are used in this experiment) Nernst equation takes form

$$\varphi_{Me^{n+}/Me^0} = \varphi^0_{Me^{n+}/Me^0} + \frac{0.059}{n} \lg[Me^{n+}]. \tag{8.4}$$

Electrochemical corrosion

Corrosion of metals is the process of spontaneous metal deterioration as a result of chemical interaction with components of its surroundings.

Chemical corrosion occurs at high temperatures, when no liquid water is present in the system, as a result of metal interaction with an aggressive oxidizer, e.g. F_2, Cl_2, O_2, SO_2; essentially, it is a direct transfer of electrons between metallic atoms and the oxidizing agent.

Metal parts of an equipment working at elevated temperatures are typical targets of chemical corrosion. These include internal combustion engines, turbines, furnaces, heat exchangers etc. Examples may range from simple combustion

$$4\,Fe + 3\,O_2 = 2\,Fe_2O_3$$

to more complex processes involving additional chemical species, e.g.

$$2\,Fe + O_2 + 2\,H_2S = 2\,FeS + 2\,H_2O;$$

$$2\,Fe + O_2 + 3\,SO_2 = Fe_2(SO_4)_3.$$

In many cases products of the chemical corrosion form dense impermeable films on the surface of the metal that impede chemical corrosion.

*square braces in the following equations denote equilibrium concentration of chemical species

Electrochemical corrosion is the process of spontaneous metal oxidation in humid air or electrolite solution as a result of forming and functioning of corrosive electrochemical cells.

A special characteristic of the process is that metal oxidation (*anode*, "–") and oxidizer reduction (*cathode*, "+") subprocesses occur at separate locations, thus it is associated with the electric currents inside the metal.

When metals with different activity come into contact, **contact corrosive galvanic cell** is formed:

(–): more active metal | H_2O, electrolyte | less active metal **:(+)**

Metal activity in contact with electrolyte solution is determined by its standard electrode potential: the more active is the metal, the less is the value of electrochemical potential. For example, iron is a more active metal than lead, because it has larger standard electrode potential value:

$$\varphi^{\circ}_{Fe^{2+}/Fe^0} = -0.44 \text{ V}, \ \varphi^{\circ}_{Pb^{2+}/Pb^0} = -0.13 \text{ V},$$

thus

$$\varphi^{\circ}_{Pb^{2+}/Pb^0} > \varphi^{\circ}_{Fe^{2+}/Fe^0}.$$

Consider a construction formed by iron and lead presses together in an acidic solution containing oxygen. The scheme of a corrosive cell is:

$$(-) \quad \text{Fe} \,|H^+, \underset{\text{pH} < 7}{O_2, \ H_2O} \,| \,\text{Pb} \quad (+)$$

Corrosion will occur if the potential of the cathode subsystem is greater than the potential of the anode. Cathode subsystem potential in oxygen containing environments can be calculated using the *Nernst equation for the oxygen electrode*:

$$\varphi_{O_2, \ Me/H_2O} = 1,23 - 0,059\text{pH}.$$

Taking the pH of the acidic solution to be pH = 5:

$$\varphi_{O_2, \ Me/H_2O} = 1,23 - 0,059 \cdot 5 = 0,395 \text{ V} > \varphi^{\circ}_{Fe^{2+}/Fe^0} = -0.44 \text{ V}.$$

Thus, the condition for iron corrosion is satisfied, and following chemical reactions occur in the corrosive cell as a result of its operation:

$$\begin{array}{lll} \textit{Anode}: & \text{Fe} \longrightarrow \text{Fe}^{2+} + 2\,\text{e}^- & | \times 2 \\ \textit{Cathode}: & \text{O}_2 + 4\,\text{H}^+ + 4\,\text{e}^- \longrightarrow 2\,\text{H}_2\text{O} & | \times 1 \end{array}$$

Combination of the two equations produces the spontaneous (in the present case) RedOx reaction which leads to the metal corrosion:

$$2\,Fe + O_2 + 4\,H^+ \longrightarrow 2\,Fe^{2+} + 2\,H_2O.$$

In neutral environment (aqueous solutions of non-hydrolyzing salts, e.g. KCl, $NaNO_3$, K_2SO_4) corrosion proceeds as follows:

$$(-) \quad Fe\,|O_2,\ \underset{pH\,=\,7}{H_2O},\ KCl\,|\,Pb \quad (+),$$

$$\begin{array}{lll} \textit{Anode}: & Fe \longrightarrow Fe^{2+} + 2\,e^- & |\times 2 \\ \textit{Cathode}: & O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^- & |\times 1 \\ \hline & 2\,Fe + 2\,H_2O + O_2 \longrightarrow 2\,Fe(OH)_2. & \end{array}$$

Iron (II) hydroxide is further oxidized to form iron (III) hydroxide:

$$4\,Fe(OH)_2 + O_2 + 2\,H_2O \longrightarrow 4\,Fe(OH)_3$$

As can be seen from the above examples, molecular O_2 is spent during the corrosion in oxygen containing environments.

In environments where oxygen is absent for some reason, corrosion produces molecular hydrogen H_2. In such a case corrosion occurs when

$$\varphi_{Me^{n+}/Me^0} < \varphi_{H^+/H_2,\,Me} = -0,059pH.$$

The anode and cathode processes may be represented by the equations:

$$\begin{array}{ll} \textit{Anode}: & Me^0 \longrightarrow Me^{n+} + ne^- \\ \textit{Cathode}: & 2\,H^+ + 2\,e^- \longrightarrow {H_2}^0\ (pH < 7),\ \text{or} \\ & 2\,H_2O + 2\,e^- \longrightarrow {H_2}^0 + 2\,OH^-\ (pH \geq 7). \end{array}$$

Electrochemical corrosion can also occur when there is no contact of several metals. Impurities more stable against oxidation* function as cathodes in microscopic corrosive cells:

$$(-) \quad Me\,|H_2O,\ O_2|\,\text{Impurities} \quad (+)$$

Other reasons that may lead to the electrochemical corrosion of metals include anisotropic properties of their crystals, variation of physical conditions on different areas of a metal, inhomogeneity of a corrosive environment (e.g. variable concentration of ions in an electrolyte), mechanical deformation etc.

*Examples include borides, carbides, silicides etc.

Electrolysis

Electrolysis RedOx reactions that occur on electrodes connected to a constant current source, as a result of electric current through a salt solution or melt.

Electrolysis is most often conducted with *inert electrodes* that do not change during the process*. An electrode connected to a negative terminal of a constant current source, which is called a *cathode*, passes an electron to oxidizer; thus, *reduction* takes place on the cathode. An *anode* is an electrode connected to a positive terminal of the constant current source on which reducing agent oxidizes by loosing electrons to an electric circuit.

Several competing processes must be considered to predict the products of electrolysis: water molecules may be reduced on the cathode as well as metal cations; similarly, anions or water may oxidize on the anode. Reduction of water molecules on the cathode is possible in a range of potentials from -1,6 V through -0,24 V. Thus, metal ions can be divided into three groups by their ability to compete with water:

- Metal cations with potentials much smaller than -1,6 V are weaker oxidizers than water and only the latter is reduced on the cathode, producing hydrogen:

$$2\,H_2O + 2\,e^- \longrightarrow {H_2}^0\uparrow + 2\,OH^-.$$

- Metal cations with potentials greater than -0,24 V are stronger oxidizers than H_2O molecules, and they are reduced on the cathode during electrolysis, producing metals:

$$Me^{n+} + ne^- \longrightarrow Me^0.$$

- Cations of metals having oxidizing power similar to that of water (the range of potentials from -1,6 V through -0,24 V) are reduced along the water:

$$\begin{aligned} Me^{n+} + ne^- &\longrightarrow Me^0 \\ 2\,H_2O + 2\,e^- &\longrightarrow {H_2}^0\uparrow + 2\,OH^-. \end{aligned}$$

Anode processes are ranged as follows:

- Single-atom anions, such as Cl^-, Br^-, I^-, S^{2-}, are stronger reducing agents that H_2O; therefore, only they are oxidized on the anode:

$$\begin{aligned} 2\,Hal^- &\longrightarrow {Hal_2}^0 + 2\,e^-; \quad \text{Hal=Cl, Br, I} \\ S^{2-} &\longrightarrow S^0 + 2\,e^-. \end{aligned}$$

*Examples of such electrodes are Pt, Pd metals, graphite (carbon), PbO_2 etc.

- Polyatomic anions containing oxygen (ClO_4^-, NO_3^-, PO_4^{3-}, CO_3^{2-}, SO_4^{2-}) and F^- are weaker reducers than water molecules and never oxidize on the anode; water molecules are oxidized instead:

$$2\,H_2O \longrightarrow O_2^0\uparrow + 4\,H^+ + 4\,e^-.$$

When a metal with stronger reduction ability than water molecules or anions in solution is used as the anode material, this metal will oxidize, releasing its ions into the solution:

$$Me^0 \longrightarrow Me^{n+} + ne^-.$$

This is the case of *electrolysis with a soluble anode*. Newly created cations are attracted to the cathode, where they are reduced to form pure metal:

$$Me^{n+} + ne^- \longrightarrow Me^0.$$

Pocedure

Materials and equipment

Equipment: voltmeter, glass and clay beakers, copper and zinc plates, abrasive paper, filtering paper, a rack with test tubes, U-shaped glass electrolyzer with carbon electrodes, constant current source.

Chemicals: copper and zinc electrolyte solutions

Copper sulfate solutions	Zinc sulfate solutions
CuA: $[Cu^{2+}] = 0,158$ mol/l	ZnA: $[Zn^{2+}] = 0,71$ mol/l
CuB: $[Cu^{2+}] = 5,89 \cdot 10^{-3}$ mol/l	ZnB: $[Zn^{2+}] = 7,35 \cdot 10^{-3}$ mol/l
CuC: $[Cu^{2+}] = 7,35 \cdot 10^{-5}$ mol/l	

iron wire (iron paper clips), coper, zinc, and tin pieces, $K_3[Fe(CN)_6]$* aqueous solution, sulfuric acid aqueous solution with $c(H_2SO_4) = 0{,}1$ mol/l; steel plate, aqueous solution of 10 g of $K_3[Fe(CN)_6]$, 20 g of NaCl, 10 g of gelatin, and 1 ml of phenolphthalein per liter of water (corrosive solution); aqueous solutions of potassium iodide ($c(KI) = 0,1$ mol/l), copper sulfate ($c(CuSO_4) = 0,25$ mol/l) and phenolphthalein.

*The reagent has modern name potassium hexacianoferrat (III), but it was called Prussian red or red blood salt in the past. The latter name represents its obsolete production method—from cattle's blood in slaughterhouses.

Experimental

Galvanic cell

1. Get an assignment from instructor (code of copper and zinc sulfate solutions, i.e. CuA, ZnB) and write them down into your report together with solutions concentration.
2. Calculate equilibrium electrode potentials of zinc and copper electrodes (eq. 8.4) with the concentration of metal cations given in the assignment; compare the values and determine which electrode is cathode and which is anode.
3. Compose a scheme of the copper-zinc galvanic cell* and write down electrode processes (see eq. 8.1 and immediately below it).
4. Construct the galvanic cell according to the previously derived scheme. To do that pour anode solution into glass beaker and cathode into clay; connect anode and cathode metallic plates to a voltmeter and put them into their electrolytes (solutions); put clay beaker with electrolyte and a plate into the electrolyte in glass beaker.
5. Measure a voltage that appears on the voltmeter and write it down into the report.
6. Compute the *electromotive force* of the galvanic cell (eq. 8.2).
7. Compute the *polarization* of the galvanic cell (eq. 8.3)

Electrochemical corrosion

The influence of the contacting metals on the rate of corrosion. Pour several milliliters of H_2SO_4 solution into each of three test tubes and add several droplets of $K_3[Fe(CN)_6]$ solution†.

Simultaneously immerse iron paper clips connected with various metals into the tubes as follows:

- iron–copper into the first tube;
- iron–tin into the second tube;
- iron–zinc into the third tube.

Observe the appearance of bulbs of gas. What gas is this? On which of the metals the process occurs in each case? Compare the intensities of the processes for each metal pairs. In about two minutes after immersion compare the rates of iron deterioration between the pairs by the intensity of Turnbull's blue. Write down the schemes of corrosive cells

*this cell is also often called Daniel's cell or Daniel-Jacoby cell

†potassium hexacianoferrat (III) is a sensitive reagent for Fe^{2+} ions; the product of their interaction is Turnbull's blue:

$$3\,Fe^{2+} + 2\,\underset{\text{light yellow}}{[Fe(CN)_6]^{3-}} \longrightarrow \underset{\text{intense blue}}{Fe_3[Fe(CN)_6]_2}.$$

and the reactions on the electrodes. Which of the metals provides iron with corrosion protection?

Atmospheric corrosion of steel. Polish the steel plate with abrasive paper. Soak the filtering paper with the corrosive solution, and apply it tho the polished steel surface (provide a good contact between the paper and the surface by pressing them together). In 3–5 minutes remove the paper and observe pink (fuchsia) and blue areas on its surface. Write down the scheme of the corrosive cells, the reactions on the electrodes, and determine which of the colored areas indicate cathode and anode regions.

Electrolysis

Electrolysis of KI. Fill the electrolyzer with potassium iodide and add 5–6 drops of phenolphthalein into each end. Immerse the electrodes into the solution and connect them to the constant current source with voltage of 4–6 V; keep the current flowing for several minutes. Observe the color change in the cathode and anode regions. Write down equations of the processes on both electrodes and the products that were formed.

Electrolysis of copper sulfate. Fill the electrolyzer with $CuSO_4$ solution, insert the electrodes and apply the current. Observe the formation of gas bulbs on one electrode and deposition of the metal on the other. Which electrode is the anode and which is the cathode? Write down equations of the processes on the electrodes.

*Electrolysis with a soluble anode.*Exchange the terminals on the constant current source to which the electrodes are attached in the previous installment, so that the electrode with copper deposition is connected to the negative terminal. This electrode is effectively turned into the soluble anode. Observe processes on the electrodes, explain copper dissolution, and write down equations of the processes.

Conclusions

TIP
Try to answer this questions in your conclusion:

- How do we determine which electrode is the cathode and which is the anode?
- What makes electrons move through the circuit of the galvanic cell?
- Why does voltage in a galvanic cell always differ from the electromotive force?

- When does the corrosion of metals occur?
- If two metals are in contact in corrosive environment, which of them will deteriorate?

- Why does steel corrode in atmospheric environment? Will the process occur in river water or soil? Why?

- What is electrolysis and what are the conditions for it to occur?
- Why do several processes compete between each other on the electrodes?
- How does the material of an electrode change in case of electrolysis with inert electrodes? In case of soluble anode?